Extending the CCW EOS: Extending the Nuclear Contribution to High Temperatures

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This is a progress report on our efforts to apply the results summarized in [1] to make new equations of state (EOS) and to generate new tables for the SESAME database. In our initial work, reported in [2] and last year's volume, we described a theory that is applicable at all densities above ρ_{ref} and at all temperatures below roughly five times the melting temperature, at which point the nuclear motion becomes gaslike and renders our liquid theory inapplicable. Since a typical SESAME EOS [3] covers compressions from 10^{-4} to 10^{4} and temperatures up to 10^{5} eV, to construct SESAME EOS using this theory we must consider how to extend its range of validity substantially. This requires meeting two challenges: (1) extend the EOS to higher densities, where density functional theory (DFT) and experimental results are not available but the theory is still sound, and (2) extend the theory itself to high temperatures, where the nuclear motion becomes gaslike, and to densities below ρ_{ref}.

Last year we solved most of the first problem, providing techniques to extend the melt curve, solid and liquid cold curves, and solid and liquid nuclear contributions to arbitrary density. Here we report our progress on the second challenge, extending the theory; we will also summarize the problems that remain.

Our underlying strategy remains the same as in [2]: relying on basic condensed matter theory and observed trends in low-compression material behavior, we concluded that a generic material under extreme conditions will be a structureless metal crystal that melts normally to a metal liquid; we then develop interpolations between our original EOS and this high-compression and high-temperature state. By doing so, we incorporate the best physics in each region of temperature and compression.

Before extending the nuclear theory to high temperatures, we decided to incorporate into the low-temperature liquid theory [4] a phenomenological treatment of the "boundary term" in the free energy, the term that accounts for the fact that the potential valleys in which the system moves in the liquid state have boundaries that the liquid probes in its motion. While we do not have a detailed theory for this term, its effects on the free energy of a liquid are considerable. Experimental results for C_V of nine liquid metals at atmospheric pressure and temperatures up to five times melting are well fit by the expression

$$C^{l}_{ph} = 3k\left[\frac{T}{T_m}\right]^{-\alpha} \tag{1}$$

where k is Boltzmann's constant, T_m is the melting temperature, and $\alpha = 0.17$ best fits the data. (See Fig. 1.) We determined the free energy that produces this specific heat and that equals the no-boundary-term liquid free energy at melt, and we used it as our low-temperature free energy for the liquid.

To determine the nuclear free energy at high temperature, we used the expression from pseudopotential perturbation theory,

$$F^{g}_{nuc}(\rho,T) = \Omega(\rho) + kT\left[\ln\left(\frac{\rho\Lambda^3}{M}\right) - 1\right] + \frac{1}{2}\langle\varphi\rangle\ , \tag{2}$$

where the Ω term is responsible for metallic binding, φ is the interatomic potential, M is the atomic mass, and Λ is the thermal de Broglie wavelength. By examining the relative sizes of the terms in Eq. 2, we were able to argue that the middle term was by far the largest, so only it needed to be retained in our theory.

Just as at low temperatures, the high-temperature theory contains a term we have neglected up to this point: the effect of interactions between the motion of the

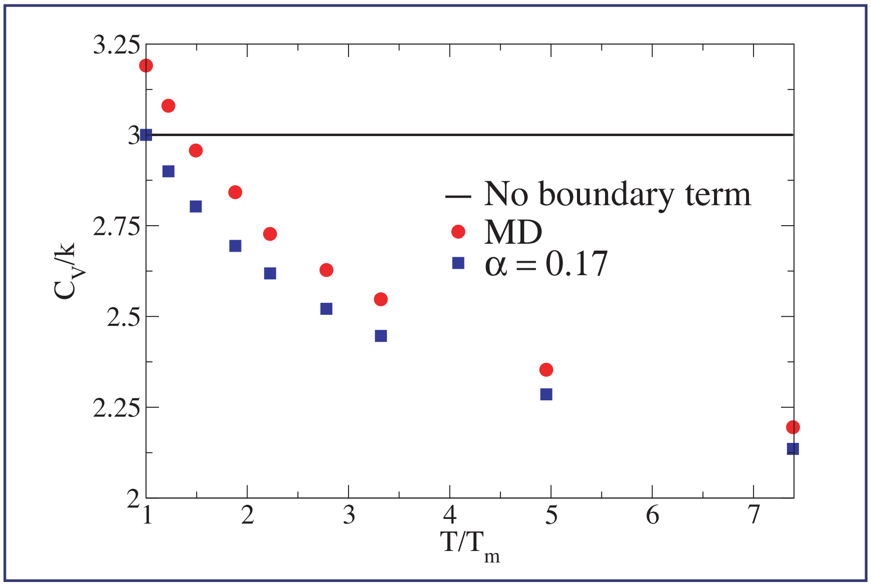

Figure 1—
The nuclear contribution to C_V for pseudopotential sodium at $\rho = 1.0063$ g/cm^3 as a function of T/T_m. The solid line is $C_V = 3k$, the prediction of the liquid theory without any boundary term. The circles are molecular dynamics (MD) results, and the squares are values from Eq. 1 with $\alpha = 0.17$ evaluated at the same points. The difference between the MD and Eq. 1 is due to anharmonicity, which is present in the MD and slowly approaches zero as T increases.

nuclei and thermal excitation of the electrons. At low temperatures, it can be shown that this term is much smaller than the electronic contribution, but at high temperatures that argument fails. However, we were able to argue that at high temperatures this term is much smaller than the nuclear contribution we considered in the previous paragraph, so it remains negligible at high temperatures, just as at low temperatures, but for a different reason.

Finally, we constructed interpolation formulas between the low- and high-temperature forms for the nuclear free energy as follows. We defined the nuclear free energy to be

$$F_{nuc} = \chi \, F^{l}_{ph} + (1-\chi) F^{g}_{nuc} \qquad (3)$$

where F^{l}_{ph} is the liquid free energy including boundary effects constructed at the beginning, F^{g}_{nuc} is the high-temperature nuclear term we just considered, and the function χ monotonically decreases from 1 at $T = T_m$ to zero as T goes to infinity, with the first two temperature derivatives vanishing at T_m. This guarantees that the new F_{nuc} reproduces the old liquid free energy and thermodynamic functions at T_m while approaching the high-temperature free energy as T increases.

The only remaining tasks are (a) to extend the electronic contribution to high compressions and temperatures, and (b) to extend the full theory to densities below ρ_{ref}.

Details of this work can be found in [5].

[1] D.C. Wallace, *Statistical Physics of Crystals and Liquids* (World Scientific, Singapore, 2002).
[2] E.D. Chisolm, S.D. Crockett, and D.C. Wallace, "Extending the CCW EOS I: Extending the Cold and Nuclear Contributions to High Compression," Los Alamos National Laboratory report LA-UR-03-7344 (Oct. 2003).
[3] S.P. Lyon and J.D. Johnson, "T-1 Handbook-Sesame Equation of State Library Volumes 1 and 2 (Public Version)," Los Alamos National Laboratory report, LA-UR-99-3900 (July 1999).
[4] E.D. Chisolm and D.C. Wallace, *J. Phys.: Condens. Matter* **13**, R739 (2001).
[5] E.D. Chisolm and D.C. Wallace, "Extending the CCS EOS II: Extending the Nuclear Contribution to High Temperatures," Los Alamos National Laboratory report LA-UR-04-3948 (June 2004).

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